Benzenehexathiol as a Template Rim for a Golden Wheel: Synthesis and Structure of [{CSAu(PPh$_3$)}$_6$]

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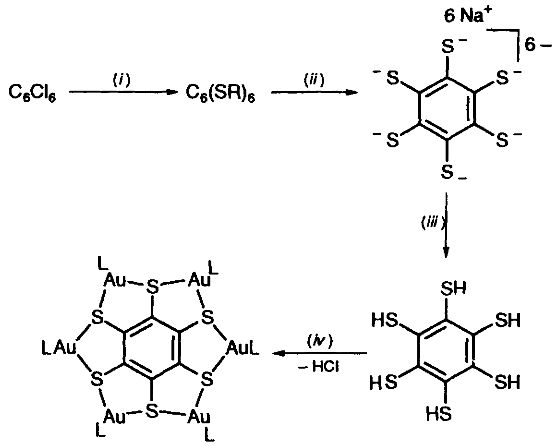
The reaction of benzenehexathiol, $C_6(SH)_6$, with [Au(PPh$_3$)Cl] in the presence of triethylamine gave the hexanuclear gold(I) compound [{CSAu(PPh$_3$)}$_6$] whose structure has been determined; the hexagon of the central benzene carbon atoms is surrounded by a hexagon of sulfur atoms, followed by a hexagon of gold atoms and the wheel-like structure is completed by six peripheral phosphine ligands with interlocked aryl groups.

It was only about five years ago that benzenehexathiol was synthesized for the first time.[1a] The initial procedure[1b] leading first to the hexasodium hexathiolate *via* the hexa(isopropyl sulfide) was tedious and extremely unpleasant mainly as a result of the malodorous materials and large quantities of toxic solvents which were required. Separation of the thiolate salt proved to be difficult, and the yields variable. In subsequent studies[2-5] these difficulties were overcome by changing to the benzyl homologue. However, the properties and reactions of these interesting compounds have remained largely unexplored. This is particularly surprising since there should be enormous potential for the $C_6(SH)_6$ molecule and its anion(s) in co-ordination chemistry. As part of ongoing studies on novel gold complexes of mono- and poly-functional thiols in our laboratory and elsewhere[6-12] we have now studied the template functions of $C_6(SH)_6$ for the stereocontrolled assembly of gold.

Gold(I) thiolates with or without stabilizing phosphine ligands have a large number of applications, as exemplified by the central role of (phosphine)gold thiolates in gold therapy[13,14] and the variety of gold thiolate species in 'liquid gold' pastes used for gilding.[15] Gold–thiol interfaces are also among the most useful model systems in surface science.[16] In addition the labelling of biochemical substrates by heavy elements such as gold at sulfur centres is important for many methods of biodiagnostics.[17-19]

Benzenehexathiol, $C_6(SH)_6$, is available from C_6Cl_6 *via* $C_6(SR)_6$ (R = Pr^i or benzyl) and the hexasodium hexathiolate $Na_6(C_6S_6)$[1-5] (Scheme 1). Neither the product nor any of its precursors have been structurally characterized, but the analytical and spectroscopic data fully support the proposed formulae. Treatment of yellow $C_6(SH)_6$ (freshly prepared following a modified procedure†) with six equivalents of [Au(PPh$_3$)Cl] and triethylamine in dichloromethane at ambient temperature gives a deep red solution, from which a reddish brown product [{CSAu(PPh$_3$)}$_6$] can be isolated. The compound shows acceptable elemental analyses and exhibits a singlet at δ 35 in its ^{31}P NMR spectrum (in CHCl$_3$), which is largely independent of temperature. The FAB mass spectrum contains a series of fragment ions which can be associated with the proposed formula, but the parent ion could not be detected. The crystals show a weak red photoluminescence typical for three-co-ordinate gold(I) complexes (low wavelength UV excitation).‡



Scheme 1 R = Pr^i or benzyl, L = PPh$_3$, X = Cl (*i*) NaSR; (*ii*) Na; (*iii*) HX; (*iv*) [Au(L)Cl]

Attempts to obtain single crystals of [{CSAu(PPh$_3$)}$_6$] were only successful with filtered solutions of the primary product mixture. Very surprisingly, however, these red crystals contained [{CSAu(PPh$_3$)}$_6$] together with two moles of [NHEt$_3$]Cl (!) and four moles of chloroform.* The molecular structure is shown in Fig. 1. The molecule has a crystallographic centre of inversion at the centre of the benzene ring. This hexagon is virtually planar, but the surrounding hexagon of

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† Precursor $C_6(SCH_2C_6H_5)_6$ was synthesized from C_6Cl_6 and $Na(SCH_2C_6H_5)$ (generated *in situ* from $C_6H_5CH_2SH$ and NaH in dimethylformamide) and purified by crystallization from CDCl$_3$–MeOH in 75% yield [m.p. 125 °C; ^{13}C NMR (CDCl$_3$): δ 137.7 (CS and $C_6H_5CH_2$)]. This was converted into $Na_6(C_6S_6)$ by treatment with sodium in liquid NH$_3$ at −78 °C. Quenching with MeOH followed by degassed water and extraction with Et$_2$O gave a clear yellow aqueous solution from which large crystals separated upon cooling to 4 °C in 68% yield [^{13}C NMR (D$_2$O, 20 °C): δ 133.6 (s, CS)]. Treatment of an aqueous solution of $Na_6(C_6S_6)$ with 5% aqueous HCl (both solutions carefully deoxygenated!) gave a precipitate of $C_6(SH)_6$ (96% yield) which decomposes on heating with a change in colour, but does not melt below 400 °C [^1H NMR (CD$_3$CN, 20 °C): δ 2.14 (br s, SH)]. Correct elemental analyses obtained for $Na_6(C_6S_6)$ and $C_6(SH)_6$.

‡ Preparation of [{CSAu(PPh$_3$)}$_6$]. To a suspension of [Au(PPh$_3$)Cl] (1.00 g, 2 mmol) and $C_6(SH)_6$ (0.09 g, 0.034 mmol) in CH$_2$Cl$_2$ (30 cm^3) was added at room temperature a solution of NEt$_3$ (0.20 g, 2 mmol) in CH$_2$Cl$_2$ (20 cm^3) with stirring. The solution changed from yellow to deep red. After 2 h of continued stirring the reaction mixture was filtered and all volatiles were removed from the filtrate in a vacuum. The residue was recrystallized from CHCl$_3$–hexane (1 : 1) to give red-brown crystals. Yield 0.30 g, 30%; m.p. 245 °C with decomposition. NMR (CD$_2$Cl$_2$, 20 °C): ^1H, δ 7.02 [dd, 2 H, *J*(HH) 7.9 and 7.6, H_{meta}], 7.15 [t, 1 H, *J*(HH) 7.6, H_{para}], 7.31 [dd, 2 H, *J*(PH) 11.6 Hz, *J*(HH) 7.9, H_{ortho}]; ^{13}C, δ 129.3 [d, *J*(PC) 11.6, C_{meta}], 131.0 [d, *J*(PC) 45.0, C_{ipso}], 131.5 [d, *J*(PC) 2.2, C_{para}], 132.3 (s, CS), 134.4 [d, *J*(PC) 14.3 Hz, C_{ortho}]. Correct elemental analyses obtained.

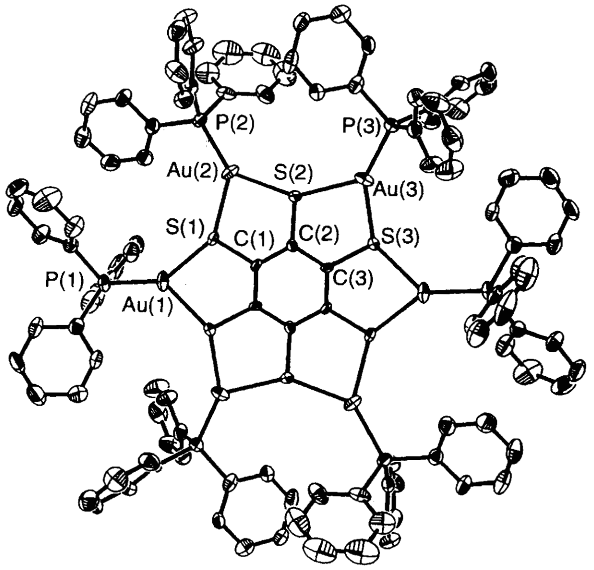

Fig. 1 Molecular structure of $[\{CSAu(PPh_3)\}_6]$ with atomic numbering (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Au(1)–S(1) 2.394(3), Au(2)–S(1) 2.447(3), Au(2)–S(2) 2.394(3), Au(3)–S(2) 2.481(3), Au(3)–S(3) 2.382(3), Au(1')–S(3) 2.469(3); Au(1)–S(1)–Au(2) 140.5(1), Au(2)–S(2)–Au(3) 142.7(1), Au(3)–S(3)–Au(1') 131.9(1), S(3')–Au(1)–S(1) 80.7(1), S(1)–Au(2)–S(2) 82.7(1), S(2)–Au(3)–S(3) 81.2(1)

sulfur atoms shows a certain puckering, which is even more pronounced with the still larger, concentric hexagon of gold atoms (Fig. 2). Two of the three crystallographically inequivalent gold atoms [Au(1), Au(3)] are above and below the best plane of carbon atoms by 0.671 and −0.561 Å, respectively, while Au(2) is very close to the molecular plane (0.067 Å). For the sulfur atoms the deviations are much smaller with −0.002 [S(1)], 0.018 [S(2)] and −0.057 Å [S(3)]. Therefore the S_6–Au_6 puckering is not following, *e.g.*, C_3 or even C_6 symmetry, as might intuitively be expected. It should be noted, however, that such symmetrical structures, or a completely planar structure, would impose a planar co-ordination on the sulfur atoms which is clearly an unfavourable configuration. The puckering of the wheel-rim is therefore the result of the tendency of the sulfur atoms to attain at least a flat pyramidal configuration. By contrast, and as expected, the configurations at the three-co-ordinated gold atoms are completely planar as evidenced by the sum of the angles at gold which are very close to 360°. The NMR of $[\{CSAu(PPh_3)\}_6]$ indicate that the molecule is fluxional in solution with virtual equivalence of all the $Au(PPh_3)$ units. None of the interatomic distances in $[\{CSAu(PPh_3)\}_6]$ is exceptional, and there are no significant sub-van der Waals contacts observed for this and the other components of the unit cell ($[NHEt_3]Cl$, $CHCl_3$).

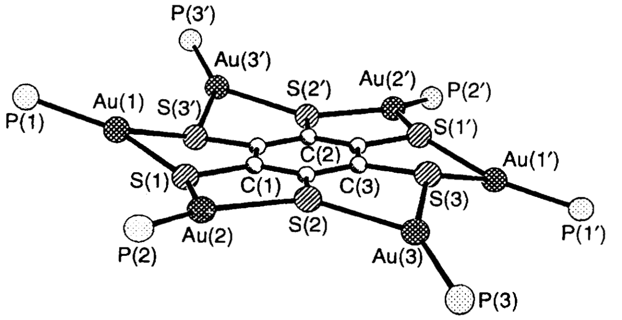

Fig. 2 Side view of $[\{CSAu(PPh_3)\}_6]$ showing the S_6–Au_6 puckering (phenyl carbon and hydrogen atoms omitted for clarity)

The results demonstrate that $Na_6(C_6S_6)$ and $C_6(SH)_6$ are excellent matrices for building co-ordination compounds with peripheral metal rings, and this concept will be pursued further. Work on polynuclear gold complexes based on dendrimers is also in progress.[21]

Acknowledgements

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[*] Crystal data. $C_{130}H_{126}Au_6Cl_{14}N_2P_6S_6$, M_r = 3772.84, red-brown crystal (0.15 × 0.30 × 0.50 mm), triclinic, space group $P\bar{1}$ (no. 2), a = 13.005(2), b = 14.691(3), c = 18.998(4) Å, α = 86.84(2), β = 73.27(2), γ = 81.53(2)°, Z = 1, D_c = 1.822 g cm^{-3}, $F(000)$ = 1818, μ(Mo-Kα) = 68.4 cm^{-1}. Enraf-Nonius CAD-4 diffractometer, graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å), θ–θ scan mode, T −68 °C. Intensity data corrected for absorption effects (ψ-scans). The structure was solved by Patterson methods and refined by full-matrix least squares (SHELXS 86, SHELXTL-PLUS).[20] Of 14 888 measured reflections 10 081 were considered 'observed' [$F_o \geqslant 4\sigma(F_o)$] and used for refinement. All non-H atoms were refined with anisotropic displacement parameters. All H-atoms were placed in calculated positions with isotropic displacement parameters (U_{iso} = 0.080 Å^2). The function minimized was $\Sigma w[(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$, $w = 1/\sigma^2(F_o)$. Final R and R' values were 0.050 and 0.058, respectively (number of refined parameters, 739). Residual electron densities were +2.43 and −2.21 e Å^{-3} (located at the gold atoms). Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.